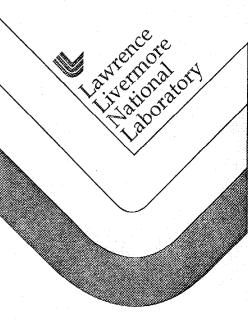
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S.M. Aceves and G.D. Berry

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# ANALYSIS OF HYDROGEN VEHICLES WITH CRYOGENIC HIGH PRESSURE STORAGE

S. M. Aceves and G. D. Berry

Lawrence Livermore National Laboratory 7000 East Ave., L-641 Livermore, CA 94551, USA saceves@llnl.gov berry6@llnl.gov

#### I. ABSTRACT

Insulated pressure vessels are cryogenic-capable pressure vessels that can be fueled with liquid hydrogen (LH<sub>2</sub>) or ambient-temperature compressed hydrogen (CH<sub>2</sub>). Insulated pressure vessels offer the advantages of liquid hydrogen tanks (low weight and volume), with reduced disadvantages (lower energy requirement for hydrogen liquefaction and reduced evaporative losses).

This paper shows an evaluation of the applicability of the insulated pressure vessels for light-duty vehicles. The paper shows an evaluation of evaporative losses and insulation requirements and a description of the current experimental plans for testing insulated pressure vessels. The results show significant advantages to the use of insulated pressure vessels for light-duty vehicles.

#### II. INTRODUCTION

Probably the most significant hurdle for hydrogen vehicles is storing sufficient hydrogen onboard. Hydrogen storage choices can determine the refueling time, cost, and infrastructure requirements, as well as indirectly influence energy efficiency, vehicle fuel economy, performance, and utility. There are at least three viable technologies for storing hydrogen fuel on cars. These are: compressed hydrogen gas (CH<sub>2</sub>), metal hydride adsorption, and cryogenic liquid hydrogen (LH<sub>2</sub>), but each has significant disadvantages.

Storage of 5 kg of hydrogen (equivalent to 19 liters; 5 gallons of gasoline) is considered necessary for a general-purpose vehicle, since it provides a 320 km (200 mile) range in a 17 km/liter (40 mpg) conventional car; or a 640 km (400 mile) range in a 34 km/liter (80 mpg) hybrid vehicle or fuel cell vehicle. Storing this hydrogen as CH<sub>2</sub> requires a volume so big that it is difficult to package in light-duty vehicles [1], and it certainly cannot be used in trucks. The external volume for a pressure vessel storing 5 kg of hydrogen at 24.8 MPa (3600 psi) is 320 liters (85 gal). Hydrides are heavy (300 kg for 5 kg of hydrogen [2]), resulting in a substantial reduction in vehicle fuel economy and performance.

Low-pressure LH<sub>2</sub> storage is light and compact, and has received significant attention due to its advantages for packaging [3]. Significant recent developments have resulted in improved safety [4, 5] and fueling infrastructure [6]. Disadvantages of low-pressure LH<sub>2</sub> storage are: the substantial amount of electricity required for liquefying the hydrogen [7]; the evaporation losses that occur during fueling low-pressure LH<sub>2</sub> tanks [8]; and the evaporation losses that occur during long periods of inactivity, due to heat transfer from the environment.

An alternative is to store hydrogen in an insulated pressure vessel that has the capacity to operate at LH<sub>2</sub> temperature (20 K), and at high pressure (24.8 MPa; 3600 psi). This vessel has the flexibility of accepting LH<sub>2</sub> or CH<sub>2</sub> as a fuel. Filling the vessel with ambient-temperature CH<sub>2</sub> reduces the amount of hydrogen stored (and therefore the vehicle range) to about a third of its value with LH<sub>2</sub>.

The fueling flexibility of the insulated pressure vessels results in significant advantages. Insulated pressure vessels have similar or better packaging characteristics than a liquid hydrogen tank (low weight and volume), with reduced energy consumption for liquefaction. Energy requirements for hydrogen liquefaction are lower than for liquid hydrogen tanks because a car with an insulated pressure vessel can use, but does not require, cryogenic hydrogen fuel. A hybrid or fuel cell vehicle (34 km/l, 80 mpg) could be refueled with ambient-temperature CH<sub>2</sub> at 24.8 MPa (3600 psi) and still achieve a 200 km range, suitable for the majority of trips. The additional energy, costs, and technological effort for cryogenic refueling need only be undertaken (and paid for) when the additional range is required for longer trips. With an insulated pressure vessel, vehicles can refuel most of the time with ambient-temperature hydrogen, using less energy, and most likely at lower ultimate cost than LH<sub>2</sub>, but with the capability of having 3 times the range of room temperature storage systems.

Insulated pressure vessels also have much reduced evaporative losses compared to LH<sub>2</sub> tanks. These results are based on a thermodynamic analysis of the vessels, and are the subject of the next section of this paper.

From an engineering and economic perspective, insulated pressure vessels strike a versatile balance between the cost and bulk of ambient-temperature CH<sub>2</sub> storage, and the energy efficiency, thermal insulation and evaporative losses of LH<sub>2</sub> storage.

## III. THERMODYNAMIC ANALYSIS

This section describes a thermodynamic model of a pressure vessel, with the purpose of calculating evaporative losses. The following assumptions are used in the analysis:

- 1. Kinetic and potential energy of the hydrogen flowing out of the vessel are neglected.
- 2. Thermal conductivity of the vessel insulation is considered to be independent of internal and external temperature.
- 3. Gaseous hydrogen is preferentially extracted from the vessels. LH<sub>2</sub> is only extracted when the amount of gaseous hydrogen is not enough to satisfy the driving requirements.
- 4. Temperature and pressure are uniform within the vessel. This assumption has recently been verified for small vessels of the size required for light-duty vehicles [9].
- 5. No conversion between the para and ortho phases of hydrogen is considered. This assumption is used because vessel temperature changes little during most operating conditions, so that the equilibrium concentration of each phase remains fairly constant. In addition to this, the para-ortho conversion is slow, with a transition time of the order of a few days [10], so that in most cases, hydrogen does not stay in the vehicle vessel long enough for any significant conversion to occur.

The first law of thermodynamics written for a pressure vessel is [11]:

$$M\frac{du}{dt} + M_v \frac{d(c_{p,v}T)}{dt} = Q - \left(\frac{p}{\rho}\right)\dot{m} \tag{1}$$

The two terms in the left-hand side of Equation (1) are the rates of change of the internal energies of the hydrogen and the vessel. Heat transfer into the vessel (Q in the equation) is positive and tends to increase the temperature of the vessel. However, the last term in the right hand side of Equation (1) represents a cooling effect on the vessel, when mass is extracted ( $\dot{m}>0$ ). Considering that the density of hydrogen is very low, this term is often significant. The last term in Equation (1) is commonly known as the flow work, since it is the work that the hydrogen stored in the vessel has to do to push out the hydrogen being extracted.

Equation (1) is solved for a low-pressure LH<sub>2</sub> storage and for the insulated pressure vessel. The equation is solved iteratively with a computer program which includes subroutines for calculating hydrogen properties. The required property values are obtained from McCarty [12]. The specific heat of the vessel materials,  $c_{p,v}$  is obtained as a function of temperature from correlations given in the literature [13].

## IV. VESSEL CHARACTERISTICS

This paper considers three vessels, described as follows:

- 1. A conventional, low-pressure LH<sub>2</sub> tank with a multilayer vacuum superinsulation (MLVSI) and 0.5 MPa maximum operating pressure.
- 2. An insulated pressure vessel (24.8 MPa maximum operating pressure) with MLVSI fueled with LH2.
- 3. An insulated pressure vessel with microsphere insulation (aluminized microspheres within a vacuum) fueled with LH<sub>2</sub>.

Vessel properties are listed in Table 1. Two insulating materials (MLVSI and microspheres) are used in the analysis to study the effect of insulation level on hydrogen losses. No low-pressure LH<sub>2</sub> tank with microsphere insulation is studied in this paper, because low-pressure LH<sub>2</sub> tanks are very sensitive to heat transfer from the environment. According to Bunger and Owren [9], LH<sub>2</sub> poses requirements that are beyond the thermal performance of current vacuum powder insulation.

All vessels are designed to store 5 kg of hydrogen. The weight of the vessels, accessories, insulation, and external cover are calculated from data given by [14]. The vessels are assumed to have a cylindrical shape with hemispherical ends, and the length of the cylindrical segment is assumed to be equal to the diameter. Insulation

properties are obtained from [9], which lists ranges of measured conductivity. Worst-case (highest) conductivity values are selected from these ranges.

The heat transfer rate, Q, has two components: heat transfer through the insulation, and parasitic heat transfer. Heat transfer through the insulation is assumed proportional to the temperature difference between the environment and the hydrogen inside the vessel. Parasitic heat transfer takes into account heat transfer through accessories, connecting lines, etc., and is assumed constant and equal to 0.5 W for a 2 cm insulation thickness.

This paper considers the application of hydrogen vessels to two vehicles: a hydrogen vehicle with a 17 km/liter (40 mpg) gasoline-equivalent fuel economy [15]; and a high efficiency hybrid or fuel cell car with a 34 km/l (80 mpg) gasoline equivalent fuel economy [16]. The results can be easily scaled for application to vehicles with any other fuel economy.

#### V. RESULTS

Figure 1 shows hydrogen losses during operation. The figure assumes that the vessels are filled to full capacity (5 kg), and then the vehicles are driven a fixed distance every day. The figure shows total cumulative evaporative hydrogen losses out of a full tank as a function of the daily driving distance. The figure includes information for 17 km/l and 34 km/l cars respectively in the lower and upper x-axes. The figure shows that a low-pressure LH<sub>2</sub> tank loses hydrogen even when driven 50 km per day in a 17 km/l car (100 km in a 34 km/l car). Losses from a low-pressure LH<sub>2</sub> tank grow rapidly as the daily driving distance drops. Insulated pressure vessels lose hydrogen only for very short daily driving distances. Even a microsphere-insulated vessel does not lose any hydrogen when driven 10 km/day or more (20 km/day in the 34 km/l car). Since most people drive considerably more than this distance, no losses are expected under normal operating conditions.

Figure 2 shows losses for a parked vehicle. The figure shows cumulative hydrogen losses as a function of the number of days that the vehicle remains idle. The most unfavorable condition is assumed: the vehicles are parked immediately after fueling. The low-pressure LH<sub>2</sub> tank has 2 days of dormancy (2 days without fuel loss) before any hydrogen has to be vented. After this, losses increase quickly, and practically all of the hydrogen is lost after 15 days. This may represent a significant inconvenience to a driver, who may be unable to operate the vehicle after a long period of parking. Insulated pressure vessels have a much longer dormancy (up to 16 days). Total losses for the insulated pressure vessel with MLVSI is only 1 kg after 1 month of parking. In addition to this, insulated pressure vessels retain about a third of their total capacity even when they reach thermal equilibrium with the environment after a very long idle time, due to their high pressure capacity, therefore guaranteeing that the vehicle never runs out of fuel during a long idle period.

Figures 1 and 2 show a comparison in thermal performance for insulated pressure vessels and LH<sub>2</sub> tanks with equal insulation thickness (2 cm). Another important aspect of the comparison consists of determining the required insulation thickness for a LH<sub>2</sub> tank to have the same thermal performance as an insulated pressure vessel. This is illustrated in Figure 3. Figure 3 shows the effect of changing the insulation thickness on the thermal performance of an LH<sub>2</sub> tank. The figure shows the dormancy (number of days before any fuel loss occurs in a parked vehicle), and the minimum daily driving distance required for obtaining zero fuel losses, both as a function of the insulation thickness. The analysis assumes that the heat transfer through accessories is inversely proportional to the insulation thickness, so that it drops from the base-case value of 0.5 W for a thickness of 2 cm to 0.05 W at 20 cm thickness. The figure shows two diamond-shaped symbols, which indicate the corresponding dormancy (16 days, from Figure 2) and the daily driving distance for no losses (3 km/day, from Figure 1), for an insulated pressure vessel with 2 cm of MLVSI. The figure shows that, to achieve the same thermal performance as the insulated pressure vessel, an LH<sub>2</sub> tank requires either 13 or 20 cm of MLVSI. An insulation thickness of 13 cm is required to obtain the same period of parking without losses, and 20 cm are necessary to obtain the same minimum daily driving distance for no losses.

The big insulation requirements for LH<sub>2</sub> tanks with the same thermal performance as insulated pressure vessels have a major effect on external volume. Figure 4 shows internal and external volume for the insulated pressure vessel and LH<sub>2</sub> tank with 2 cm of MLVSI, and for LH<sub>2</sub> tanks with the same dormancy, and the same daily driving distance for no losses. It is clear that the vessels with equal thermal performance as the insulated pressure vessels are impractical due to their large volume. As a conclusion it can be said that insulated pressure vessels are a substantially more compact storage technology than LH<sub>2</sub> tanks, when vessels with equal thermal performance are compared.

## VI. EXPERIMENTAL TESTING OF INSULATED PRESSURE VESELS

The analysis presented in this paper has assumed that insulated pressure vessels can be built to withstand the thermal stresses introduced when an initially warm vessel is filled with LH<sub>2</sub>. Ideally, it would be desirable to use regular aluminum-lined, fiber-wrapped pressure vessels directly from the production line to avoid the cost of special designs, even though these vessels are not designed for many low-temperature cycles. While the applicability of these vessels for LH<sub>2</sub> fueling in vehicles has not been demonstrated (to the authors' knowledge), an experiment has been carried out [17] in which carbon fiber-aluminum and kevlar-aluminum vessels were cycled over a limited number of cycles (17) at LH<sub>2</sub> temperature. The vessels were burst-tested after cycling. The results of the experiment showed that there was no performance loss due to cycling. This experiment indicates that it may be possible to use regular fiber-wrapped aluminum vessels for operation at LH<sub>2</sub> temperature and high pressure. However, additional cyclic testing is necessary, because a vehicle requires many more than 17 fueling cycles.

To accomplish the required testing, an experimental setup has been built inside a high-pressure cell. A schematic is shown in Figure 5. The plan consists of running the vessels through 1000 high-pressure cycles and 100 low-temperature cycles. The cycles are alternated, running 10 pressure cycles followed by a temperature cycle, and repeating this sequence 100 times. This test is expected to replicate what would happen to these vessels during operation in a hydrogen-fueled car. Vessels will then be burst-tested, to evaluate any reduction in safety factor due to cycling. Further experiments will include a test of the vessel insulation, and instrumentation for measuring pressure, temperature and level.

#### VII. CONCLUSIONS

This paper shows that insulated pressure vessels have good packaging characteristics and themal performance compared to LH<sub>2</sub> tanks, and also a potential for reduced energy required for hydrogen liquefaction. For these reasons, they are considered to be a good alternative for hydrogen storage. The most important results can be summarized as follows:

- Insulated pressure vessels do not lose any hydrogen for daily driving distances of more than 10 km/day for a 17 km/l energy equivalent fuel economy. Since almost all cars are driven for longer distances, most cars would never lose any hydrogen.
- 2. Losses during long periods of parking are small. Due to their high pressure capacity, these vessels retain about a third of its full charge even after a very long period of inactivity, so that the owner would not risk running out of fuel.
- 3. Insulation of an LH<sub>2</sub> tank has to be between 6.5 and 10 times thicker than for an insulated pressure vessel to achieve equal thermal performance. Considering the large volume occupied by such a thick insulation layer, insulated pressure vessels are a more compact storage technology than LH<sub>2</sub> tanks, for equal thermal performance.
- 4. Previous testing has determined the potential of low-temperature operation of conventional aluminum-lined wrapped vessels for a limited number of cycles. Further testing will extend the number of cycles to the values required for a light-duty vehicle.

#### VIII. NOMENCLATURE

- c<sub>p,v</sub> specific heat of the vessel enclosed within the insulation
- *m* mass flow rate of hydrogen extracted from the vessel
- M total mass of hydrogen stored in the vessel
- My mass of the vessel enclosed within the insulation
- p pressure
- O heat transfer rate from the environment into the vessel
- t time
- T temperature
- u specific internal energy of hydrogen
- ρ density of the hydrogen leaving the vessel

### IX. ACKNOWLEDGMENTS

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#### REFERENCES

- [1] Pentastar Electronics, 1997, "Direct-Hydrogen-Fueled Proton-Exchange-Membrane Fuel Cell System for Transportation Applications, Conceptual Design Report," Report DOE/CE/50390-9, prepared for U.S. Department of Energy, Office of Transportation Technologies, under contract DE-AC02-94CE50390.
- [2] Michel, F., Fieseler, H., Meyer, G., and Theissen, F., 1996, "Onboard Equipment for Liquid Hydrogen Vehicles," Proceedings of the 11<sup>th</sup> World Hydrogen Energy Conference, Stuttgart, Germany, pp. 1063-1077.
- [3] Braess, H.H., and Strobl, W., 1996, "Hydrogen as a Fuel for Road Transport of the Future: Possibilities and Prerequisites," Proceedings of the 11<sup>th</sup> World Hydrogen Energy Conference, Stuttgart, Germany.
- [4] Pehr, K., 1996a, "Experimental Examinations on the Worst Case Behavior of LH<sub>2</sub>/LNG Tanks for Passenger Cars," Proceedings of the 11<sup>th</sup> World Hydrogen Energy Conference, Stuttgart, Germany.
- [5] Pehr, K., 1996b, "Aspects of Safety and Acceptance of LH<sub>2</sub> Tank Systems in Passenger Cars," International Journal of Hydrogen Energy, Vol. 21, pp. 387-395.
- [6] Hettinger, W. Michel, F., Ott, P., and Theissen, F., 1996, "Refueling Equipment for Liquid Hydrogen Vehicles," Proceedings of the 11<sup>th</sup> World Hydrogen Energy Conference, Stuttgart, Germany, pp. 1135-1143.
- [7] Peschka, W., 1992, "Liquid Hydrogen, Fuel of the Future," Springer-Verlag, Vienna, Austria.
- [8] Wetzel, F.J., 1996, "Handling of Liquid Hydrogen at Filling Stations," Proceedings of the 11<sup>th</sup> World Hydrogen Energy Conference, Stuttgart, Germany, pp. 1123-1134.
- [9] Bunger, U., and Owren, G., 1996, "Development Potentials for Small Mobile Storage Tanks with Vacuum Powder Insulations," Proceedings of the 11<sup>th</sup> World Hydrogen Energy Conference, Stuttgart, Germany, pp. 1043-1052.
- [10] Mathis, D.A., 1976, "Hydrogen Technology for Energy," Noyes Data Corporation, Park Ridge, NJ.
- [11] Van Wylen, G.J., and Sonntag, R.E., 1978, "Fundamentals of Classical Thermodynamics," John Wiley and Sons, New York, NY.
- [12] McCarty, R.D., 1975, "Hydrogen: Its Technology and Implications, Hydrogen Properties, Volume III," CRC Press, Cleveland, Ohio.
- [13] Scott, R.B., 1967, "Cryogenic Engineering," D. Van Nostrand Company, Inc. Princeton, NJ.
- [14] James, B.D., Baum, G.N., Lomax, F.D., Thomas, C.E., Kuhn, I.F., 1996, "Comparison of Onboard Hydrogen Storage for Fuel Cell Vehicles," Directed Technologies Report DE-AC02-94CE50389, prepared for Ford Motor Company.
- [15] Aceves, S.M., and Smith, J.R., 1996, "Lean-Burn Hydrogen Spark-Ignited Engines: The Mechanical Equivalent to the Fuel Cell," In "Alternative Fuels, Volume 3," Proceedings of the 18th Annual Fall Technical Conference of the ASME Internal Combustion Engine Division, Fairborn, OH, October 1996, pp. 23-31.
- [16] Smith, J.R., Aceves, S.M., and Van Blarigan, P., 1995, "Series Hybrid Vehicles and Optimized Hydrogen Engine Design," SAE Paper 951955, SAE Transactions, Journal of Fuels and Lubricants, Vol. 104, pp. 816-827.
- [17] Lynn, V., 1986, "Performance of Lightweight Kevlar/Aluminum Composite Pressure Vessels at Cryogenic Temperatures," Structural Composites Industries Special Report No. 86712, Pomona, CA.

Table I. CHARACTERISTICS OF THE HYDROGEN VESSELS BEING ANALYZED.

	liquid	insulated pressure vessels	
	Tank 1		Vessel 3
Mass of hydrogen stored, kg	5	5	5
Total weight, kg	21	30	30
Internal volume, liters	8.5	95	95
External volume, liters	112	144	144
Internal diameter, m	0.39	0.42	0.42
Internal surface area, m <sup>2</sup>	0.98	1.1	1.1
Aluminum mass within insulation, kg	9	10	10
Carbon mass within insulation, kg	0	10	10
Design pressure, MPa (psi)	0.5 (70)	24.8 (3600)	24.8 (3600)
Performance factor <sup>1</sup> , m (10 <sup>6</sup> in)	*	33000 (1.3)	33000 (1.3)
Safety factor	-	2.25	2.25
Insulating material	$MLVSI^2$	$MLVSI^2$	microsphere
Thermal conductivity of insulator, W/mK	0.0001	0.0001	0.0004
Insulation thickness, m	0.02	0.02	0.02
Heat transfer through accessories, W	0.5	0.5	0.5

<sup>†</sup> defined as burst pressure\*volume/weight.

2 MLVSI = multilayer vacuum superinsulation

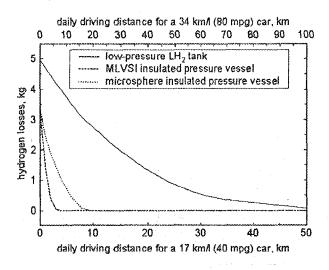


Figure 1. Cumulative hydrogen losses in kg as a function of daily driving distance, for vehicles with 17 km/liter (40 mpg); or 34 km/l (80 mpg) fuel economy, for the three vessels being analyzed in this paper.

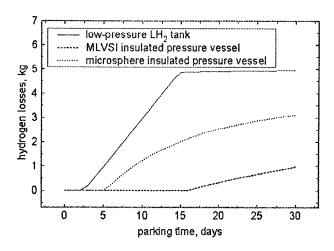


Figure 2. Cumulative hydrogen losses in kg as a function of the number of days that the vehicle remains idle, for the three vessels being analyzed in this paper, assuming that the vessels are initially full.

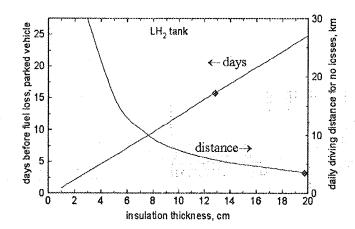


Figure 3. Dormancy and daily driving distance required for obtaining zero fuel losses, as a function of the insulation thickness, for a  $LH_2$  tank.

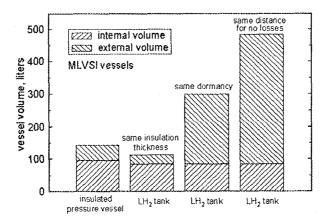


Figure 4. Internal and external volume for the base-case insulated pressure vessel and LH<sub>2</sub> tank, and for LH<sub>2</sub> tanks with same dormancy, and the same daily driving distance for no losses.

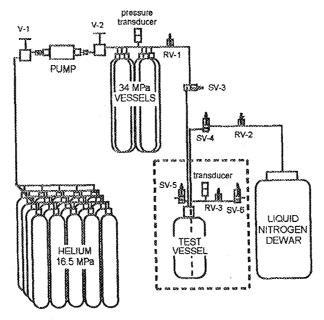


Figure 5. Schematic of the experimental setup for temperature and pressure cycling of a pressure vessel.